

# Chlorinated Degreasing Solvents: Physical-Chemical Properties Affecting Aquifer Contamination and Remediation

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## Abstract

**C**hlorinated degreasing solvents are multicomponent liquids containing not only the chlorinated hydrocarbons with which their name is associated (e.g., trichloroethylene or [TCE], perchloroethylene or [PCE], 1,1,1-trichloroethane [TCA]) but also a number of organic additives included as corrosion inhibitors and antioxidants. The additives, such as 1,4-dioxane, are likely to be of significant public-health importance as ground water contaminants due to their toxicity, solubility, and mobility. Following their use in vapor degreasing systems by industry, chlorinated degreasing solvents will also contain about 25% solubilized oil and grease.

A number of physical-chemical properties become especially important in the light of the multicomponent nature of these solvents. First, the higher aqueous solubility and lower sorption of the additives makes it is reasonable to expect that faster moving plumes of these solvent additives will precede plumes of the chlorinated hydrocarbons. Second, due to high losses of chlorinated hydrocarbons by volatilization from vapor degreasers during years in the middle of the century, it is probable that background concentrations of these hydrocarbons are present in ground water flow systems due to their downwind washout. Finally, the solubilized oil and grease may cause profound changes to the wettability of aquifer materials contacted by the solvents during their subsurface migration. It is argued, therefore, that the wettability of aquifer materials contaminated by chlorinated degreasing solvents needs to be experimentally determined before remediation of DNAPL at each site, rather than being simply assumed as water wet.

## Introduction

Chlorinated hydrocarbons were introduced into U.S. society in the early part of the 20th century. These chemicals had numerous early uses, including chemical extraction (e.g., chloroform), refrigeration (methylene chloride), and fire extinguishing (carbon tetrachloride). However, the focus of this article is on their industrial use for the solubilization of oil and grease on machined metal or nonmetal parts prior to the finishing (e.g., painting, electroplating, and etching) or assembly of the parts. This function is commonly known as "degreasing," and the chlorinated hydrocarbons used for such purposes make up the largest portion of what are referred to in this paper as chlorinated degreasing solvents. In the middle of the century, these solvents became essential to the manufacture and maintenance of aircraft, motor vehicles, machinery, computers, and the components incorporated into these products, e.g., printed circuit boards, aircraft and vehicle engines, and electric motors. Unfortunately, since 1981 (Council on Environmental Quality 1981) they have also become familiar to readers of this journal as ubiquitous ground water contaminants.

The terminology used in this paper is that employed by the University Consortium on Solvents-in-Groundwater Research Program (Feenstra et al. 1996; U.S. Environmental Protection Agency [EPA] 1992). However, it is imperative that additional terms be carefully defined. When the term "chlorinated hydrocarbon" is used, it refers only to the

<b>Table 1</b> <b>Typical Additive Concentrations in Percent by Volume Present in Vapor-Degreasing Grades of TCA for Three Industrial Societies</b>			
<b>Additive</b>	<b>United States</b>	<b>Europe</b>	<b>Japan</b>
1,2 Butylene oxide	0.5–0.8	0.6–1.0	0.1–0.6
Nitromethane	0.4–0.7	0.4–1.0	0.1–0.4
1,4-Dioxane	2.0–3.5	3.5	3.5
<i>sec</i> -Butanol	1.0–2.0		
1,3-Dioxolane	1.0		
<i>tert</i> -Butanol		3.0–6.5	
Methyl butynol		2.0–3.0	
Isopropylnitrate		2.0	
Acetonitrile		3.0	
Source: Archer 1984			

chlorinated compound (e.g., TCE, PCE, CFC-113, TCA.) (It should be noted, however, that production of chlorinated hydrocarbons results in the presence of impurities arising from chemical synthesis, e.g., trace PCE in TCE). The term “chlorinated degreasing solvent” is reserved for a mixture of one or more chlorinated hydrocarbons, plus additives that act as stabilizers or inhibitors, and any solubilized hydrocarbons incorporated in the solvent during degreasing. Therefore, a chlorinated degreasing solvent is always a multicomponent liquid, as are the dense nonaqueous phase liquids (DNAPLs) that have their origin as these solvents. Finally, the term “geosystem” is used to describe the system comprising DNAPL, aquifer material, ground water, and capillary barrier (if any).

The purpose of this paper is to consider the nature of these solvents and the physical-chemical processes that affect aquifer contamination and remediation. The first topic considered is the composition of chlorinated degreasing solvents as delivered to the customer, i.e., before degreasing operations. The second topic discussed is their composition and properties following vapor-degreasing operations and release to the subsurface. Thus, the first section deals with the original product, while the second deals with the product as encountered by hydrogeologists and environmental engineers in the subsurface. Finally, the implications of certain physical-chemical properties—the multicomponent solubility, volatility, and wettability with respect to aquifer material—are discussed with respect to aquifer contamination and remediation.

## The Multicomponent Nature of Chlorinated Degreasing Solvents

It is not widely appreciated by hydrogeologists that chlorinated degreasing solvents are delivered to customers containing a number of organic additives that are typically more soluble than the solvent itself. There can be little doubt that some of these additives are also more toxic than the solvent within which they are contained.

<b>Table 2</b> <b>Additives Typically Used in TCE at Concentrations of Less than 1%</b>		
<b>Chemical Type</b>	<b>Examples</b>	<b>Purpose</b>
Aliphatic amines	triethylamine, diisopropylamine	free-radical scavengers to prevent initial oxidation
Heterocyclic nitrogen compounds	pyridine, pyrrole, alkyl pyrroles	antioxidants
Substituted phenols	2-methoxyphenol, cresol	antioxidants
Oxygenated organics	1,4-dioxane, acetone, butylene oxide, propylene oxide, tetrahydrofuran, epichlorohydrin	acid acceptors
Sources: Kircher 1957; Hardie 1964; Mertens 1993; Archer 1996		

The additives are included in the solvent for three purposes (Archer 1984):

1. As an acid acceptor that reacts with and chemically neutralizes trace amounts of HCl formed during degreasing operations and which may cause corrosion of the part being degreased
2. As a metal inhibitor that deactivates the metal surface and complexes any metal salts that might form
3. As an antioxidant that reduces the solvent's potential to form oxidation products.

PCE is the only chlorinated degreasing solvent that does not require a metal inhibitor, while TCE and TCA require both metal inhibitors and acid acceptors (Dreher 1986). TCE also requires an antioxidant (Archer 1996).

These additives are known as stabilizers or inhibitors and partition between the vapor phase and boiling liquid phase in vapor degreasing systems according to their boiling points. Table 1 lists typical amounts of these additives present in various international formulations of TCA, and Table 2 lists compounds that may be present in small quantities (<1%) in TCE. Thus even “pure” TCE degreasing solvent as delivered to a factory vapor degreaser is in fact a mixture of TCE (~99%) and several additives that may pose considerable public health concerns because of their toxicity, solubility, and therefore, mobility in ground water flow systems.

## The Effects of Vapor Degreasing on Chlorinated Degreasing Solvents

The process of vapor degreasing removes the oil and grease from the surface of metal and nonmetal objects by solubilization. The vapor degreaser is a tank with a heat source to boil the solvent and a cool surface to condense the vapor in the upper section. The soiled articles are suspended in this air-free zone of solvent vapor. The hot vapor condenses onto the cool parts, dissolving oils and greases and providing a continuous rinse in clean solvent (ASTM 1989).

**Table 3**  
**Physical and Chemical Parameters for Chlorinated Hydrocarbons Used as Degreasing Solvents**

Parameter (units and source)	DCM	PCM	TCE	1,1,1-TCA	PCE	CFC-113
Liquid density (g/cm <sup>3</sup> , P&J)	1.33	1.59	1.46	1.35	1.63	1.56
Relative vapor density (20°C, P&J)	2.05	1.62	1.35	1.59	1.12	4.46
Viscosity (cP @ 20°C, P&J)	0.44	0.97	0.57	0.84	0.90	0.68 (25°C)
Aqueous solubility (mg/L @ 23–24°C, B&F)	20,000 (P&J)	780	1400	1250	240	158
Interfacial tension (dynes/cm)	28.31	45.0	34.5	29.6 (1,1,2)	47.48	47.2
Maximum contaminant level, U.S. SDWA (mg/L)	Not defined	0.005	0.005	0.200	0.005	Not defined

Sources (except where otherwise indicated): P&J = Pankow and Johnson (1996), B&F = Broholm and Feenstra (1995), all CFC-113 data from Jackson et al. (1992) and IFTs from Demond and Lindner (1993). Abbreviations: DCM = dichloromethane or methylene chloride; PCM = carbon tetrachloride or perchloromethane; TCE = trichloroethene or trichloroethylene; 1,1,1-TCA = 1,1,1-trichloroethane; PCE = perchloroethylene or tetrachloroethene; CFC-113 = chlorofluorocarbon 113 or "Freon-113" or 1,1,2-trichloro-1,2,2-trifluoro-ethane; SDWA = Safe Drinking Water Act.

**Table 4**  
**Composition and Properties of Hill AFB Operable Unit 2 DNAPL**

Component	Percent of DNAPL
TCE	53% to 65%
TCA	5% to 12%
PCE	3% to 5%
Other chlorinated degreasing solvents and oil and grease	~25%
Physical-chemical parameters	IFT ~9 dynes/cm Viscosity = 0.78 cP Density = 1.38 g/mL

Sources: Radian Corp. 1992; Oolman et al. 1995

The oil and grease being removed originates with the machining and other fabrication operations that leave machining oils, lubricants, and soldering flux (i.e., in the case of electronic components) on the surface of the part being cleaned. A properly functioning vapor degreaser will supply a clean vapor to the part being degreased. However, if the process is effective, the degreasing solvent will inevitably become contaminated with the oil and grease (or flux) from the degreasing operation. This grease will build up in the degreaser solvent and cause incomplete degreasing if not removed; this is particularly troublesome with cold cleaning. Typically, modern reference manuals recommend that the oil and grease fraction of the degreasing solvent should not exceed 25% (ASTM 1989; ASM 1994). This concentration can be determined from the boiling temperature or the specific gravity of the chlorinated degreasing solvent (ASM 1994). Older references indicate that this critical concentration might be as high as 40% (van Fossen 1944) or as low as 15% (Davidson 1938). Regardless, it would contain a significant fraction of hydrophobic compounds.

Usually, however, the solvent would be purified either in a separate still when large amounts of oil and grease have to be removed frequently, or by distillation in the degreaser itself (ASTM 1989; ASM 1994). Archer (1984)

**Table 5**  
**Specific Gravity (25°C) for Various Percentages by Volume of Oil and Grease in Four Chlorinated Degreasing Solvents**

Solvent	0%	10%	20%	30%
PCE	1.619	1.542	1.464	1.395
TCE	1.457	1.406	1.345	1.288
TCA	1.320	1.272	1.227	1.180
DCM	1.320	1.274	1.228	1.182

Source: ASM 1994

presents evidence that very soluble additives such as 1,4-dioxane tend to be concentrated in the still bottoms by in-process distillation, i.e., distillation within the degreaser itself. Evanoff (1990) indicates that in the aerospace industry the still bottoms or sludge generated by a typical in-process distillation is composed of 70% to 80% solvent and 20% to 30% oil, grease, and solids with traces of water. With respect to electronics manufacturing, he reported that the waste would be mainly high-quality CFC-113 (85% to 95%) with oil and flux (5% to 15%) and traces of water. The oil and grease from aluminum degreasing in the aerospace industry were identified by Evanoff as light hydrocarbon oils, heavier hydrocarbons, fatty acid esters, and particulate matter.

It was common practice until the 1970s that the sludge from the distillation process could usually be poured on dry ground well away from buildings, and the solvents were allowed to evaporate (ASM 1964), assuming there were no special ordinances to prevent it (they appear to have been nonexistent). The American Insurance Association (1972) even counseled that the waste should be removed to a safe location (away from inhabited areas, highways, buildings, or combustible structures) and poured onto dry sand, earth, or ashes, then cautiously ignited.

Sludge or waste solvent that was poured on dry ground and that did not evaporate or was not incinerated would constitute a DNAPL upon entering the subsurface. Table

3 presents basic data on the properties of the major chlorinated hydrocarbons used in vapor-degreasing operations. Table 4 presents the results of measurements of chlorinated degreasing solvent disposed of in chemical pits at Hill Air Force Base (AFB) in Utah and recovered as free-phase DNAPL from wells adjacent to the DNAPL entry location. Table 5 summarizes the effect of solubilized oil and grease on the specific gravity of various chlorinated degreasing solvents.

While TCE is the largest component in the DNAPL, the other components (PCE, TCA, CFC-113, and oil and grease) have significantly altered the physical-chemical properties from that of TCE. The parameter most changed is the interfacial tension (IFT) between the DNAPL and ground water which, like many other DNAPLs, is one third of the value measured for pure TCE and is much less than either PCE or TCA (Table 3). This decrease in IFT is most probably due to the incorporation of industrial detergents in the DNAPL, which act as surface-active agents and lower the IFT. Similarly the absolute viscosity is increased, no doubt due to the presence of the oil and grease incorporated in the DNAPL. The density of the DNAPL (Table 5) indicates that there is at least 5% and up to 20% oil and grease in the Hill AFB Operable Unit 2 sample.

## Physical-Chemical Properties of the Solvents and their Hydrogeological Effects

### Multicomponent Aqueous Solubility

The additives in chlorinated degreasing solvents are significantly more soluble than the chlorinated hydrocarbon themselves. This is due to the hydrophilic nature of the oxygen and amine groups in the additives (due to hydrogen bonding) and to the enhanced effect that these functional groups have on the polarity of the molecules. Table 6 lists the aqueous solubilities and octanol-water partition coefficients of several of the more toxic additives; the term "miscible" means that the compound is capable of being mixed with water in all proportions.

The dissolution of multicomponent organic liquids, such as chlorinated degreasing solvents, is known to follow Raoult's law (Bannerjee 1984; Broholm and Feenstra 1995; Jackson and Mariner 1995). Feenstra (1990) referred to the reduced solubility of a particular component from a multicomponent liquid as the effective solubility of this component, i.e.,  $C_{\text{eff}} = X_i C_s$ , where  $X_i$  is the mole fraction of the component in the liquid and  $C_s$  its aqueous solubility.

Furthermore, the mobility of a compound in aquifers is directly proportional to its solubility. This is because very hydrophilic compounds are only weakly retarded by sorption during ground water transport. For example, Schwarzenbach and Westall (1981) showed that the retardation of chlorinated benzenes was directly proportional to the octanol-water partition coefficient. Thus, TCA ( $\log K_{\text{ow}} = 2.49$ ) and TCE ( $\log K_{\text{ow}} = 2.29$ ) might be expected to travel much more slowly than the oxygenated additives listed in Table 6.

**Table 6**  
Aqueous Solubilities and Octanol-Water Partition of Some Additives Used in Chlorinated Degreasing Solvents

Additive	Log $K_{\text{ow}}$	Solubility (mg/L)
1,4-Dioxane	-0.27	Miscible
Tetrahydrofuran	0.46	Miscible
1,2-Propylene oxide	0.03	476,000
Epichlorohydrin	0.58	65,800

Source: Mackay et al. 1993

As Table 1 indicates, TCA typically contains several percent of dioxane. This cyclic ether, employed as an inhibitor to prevent corrosion of aluminum surfaces, is a probable carcinogen. The U.S. EPA (1988) estimated that 7 µg/L is the drinking water concentration that causes an increase of one case of cancer in a million people drinking 2 L of water per day for 70 years. This value is considerably less than the 200 µg/L value for TCA specified in the U.S. Safe Drinking Water Act. Because dioxane is miscible with water, it poses a significant public health risk in ground water used as drinking water sources. Furthermore, it has been found to be analytically difficult to measure at aqueous concentrations less than 150 µg/L (Lesage et al. 1990).

Lesage et al. (1990) identified dioxane as the contaminant of greatest concern at the Gloucester chemical-waste landfill near Ottawa, Ontario, Canada, because of its toxicity and solubility. While the precise origin of the dioxane is uncertain and cannot be definitively attributed to the chlorinated solvents disposed of at the landfill, the dioxane plume had migrated farther (and presumably faster) than the plumes of TCA and other chlorinated degreasing solvents mapped at the site. Figure 1 shows a cross-sectional representation of the trailing-TCA and the leading-dioxane plumes being transported through the glaciofluvial aquifer as measured in 1988. The last disposal of solvents occurred at this site in 1980, since which time dissolution of the solvents and separation of the plumes had occurred.

This pattern of dioxane leading TCA, or of other toxic additives such as butylene oxide or epichlorohydrin leading TCE, is to be expected from the release of chlorinated degreasing solvents to the subsurface. This expectation arises from the hydrophobicity-solubility relationships associated with the work of Schwarzenbach and Westall (1981) and others. Priddle and Jackson (1991) used Gloucester aquifer materials and ground water in column tests to show that the average retardation factor for dioxane was 1.1, whereas their values for 1,2-dichloroethane ( $\log K_{\text{ow}} = 1.48$ ), trichloromethane ( $\log K_{\text{ow}} = 1.97$ ), and 1,1-dichloroethene ( $\log K_{\text{ow}} = 2.13$ ) all exceeded six. Polychlorinated ethenes, such as TCE, PCE, and TCA, would be expected to be less mobile (i.e.,  $R_f > 6$ ) than any of the three chlorinated hydrocarbons tested by Priddle and Jackson (1991). Therefore the pattern of dioxane leading TCA shown in Figure 1 is not accidental,

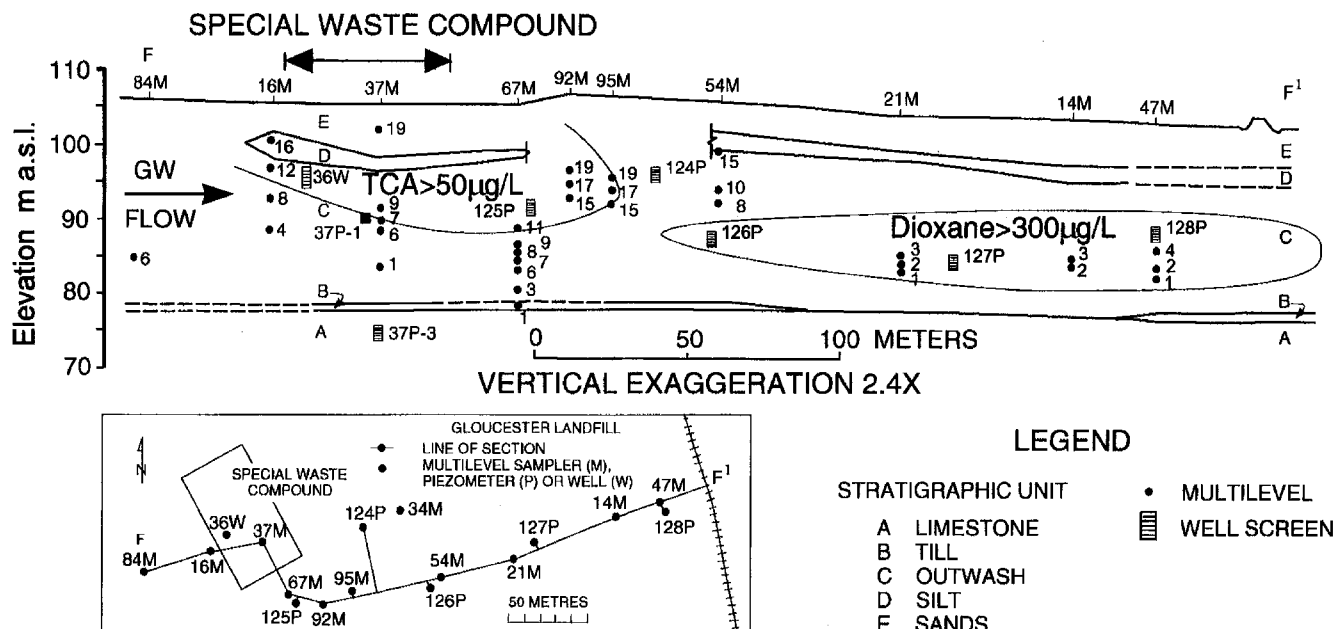


Figure 1. TCA and 1,4-dioxane plumes in 1988 at the Gloucester Landfill, Ontario, Canada (Jackson et al. 1991).

but rather the consequence of well-established principles of the mobility of organic solutes in aquifer materials.

### Volatility

Vapor losses from degreasers have been documented by the Dow Chemical Co. (Archer 1973; Skory et al. 1974). These studies indicated that emissions of solvent vapors measured one foot above the top of some 300 industrial vapor degreasers (open-top type) were 150 to 215 ppm TCE, 75 to 130 ppm TCA, and 180 to 310 ppm PCE. Because this volatilization was suspected of promoting smog formation in the Los Angeles Basin, studies were undertaken to determine the flux of chlorinated hydrocarbons in the basin. The total organic solvent emissions in July 1966 were estimated at 590 tons/day, of which 88 tons/day were halogenated compounds (Air Pollution Control District 1966). It was later estimated to be 500 tons/day, of which 25 tons were dry-cleaning fluid (i.e., PCE) and 95 tons were degreasing solvents (Simmonds et al. 1974).

These studies lead to limits on the use of TCE in Los Angeles County and later much of the United States through the Federal Clean Air Act of 1970. This had the consequence that TCE was almost entirely replaced by TCA and PCE as the chlorinated degreasing solvent of choice in Los Angeles County during 1967 through 1969 (Archer and Stevens 1977). Such large emissions meant that the lower atmosphere became contaminated with vapor-phase, chlorinated hydrocarbons. In 1972, California Institute of Technology scientists (Simmonds et al. 1974) found only traces of TCE in the air mass above the Los Angeles Basin, but measurable quantities of PCE (1.25 ppb), TCA (0.37 ppb), carbon tetrachloride (0.22 ppb), and the refrigerant trichlorofluoromethane (0.65 ppb). The California Institute of Technology group pointed out that this adventitious labeling of the Los

Angeles air mass may allow these compounds to trace the movement of air within and away from the Los Angeles Basin.

It is equally true that the inadvertent labeling of this and other air masses will result in downwind washout of these chlorinated hydrocarbons. The washout will have produced infiltration of small concentrations of chlorinated hydrocarbons in the recharge areas of ground water flow systems. Therefore, just as CFC compounds have been used for 20 years to date ground water ages (Thompson and Hayes (1979), so too might the occurrence of TCE and PCE (1940s) or TCA (1970s). However, the larger implication is that TCE, TCA, and PCE most probably have measurable background concentrations in aquifers that are downwind of those major industrial centers where vapor-degreasing operations are common, e.g., the urbanized valleys of California and the industrial cities of the Midwest.

### Wettability

The University Consortium on Solvents-in-Groundwater Research Program has maintained that most DNAPLs of interest will be nonwetting on geologic solids with respect to water, but wetting with respect to air (Feenstra et al. 1996). For example, the influential experimental work of Kueper et al. (1993) and Kueper and McWhorter (1991) is predicated on chlorinated hydrocarbons being the nonwetting phase below the water table. Recently, Powers et al. (1996) have assessed the wettability of numerous nonaqueous phase liquids (NAPLs) from various sites and of "neat solvents," including TCE, on low-organic-carbon quartz sand. The TCE was found to be strongly water wetting on the quartz sand with an advancing contact angle of 42 degrees. However, their TCE was purchased from an unidentified source and is assumed to be technical or reagent grade (i.e., essen-

tially a single component liquid) and thus would not constitute a chlorinated degreasing solvent but a chlorinated hydrocarbon as defined in this paper.

While these observations may indeed be valid for clean, unused chlorinated degreasing solvent, the solubilization of oil and grease during vapor degreasing will doubtless change the interfacial properties of the geosystem formed by DNAPL, the aquifer materials, and the ground water. Such oil and grease make the DNAPL more hydrophobic and less like the technical or reagent grade TCE tested by Powers et al. (1996) and more like the creosote and coal tar that they found to be oil wet (i.e., NAPL wet) on silica sand.

Lake (1989), discussing petroleum reservoirs, pointed out that most sandstone reservoirs tend to be water wet or intermediate wet, whereas most carbonate reservoirs tend to be intermediate wet or oil wet. DNAPL migration through a water-saturated, fractured carbonate aquifer beneath a chemical plant, as recorded by a downhole television film viewed by the authors of this article, indicated that Lake's conclusion also applies to halogenated wastes. The DNAPL, with an IFT  $\sim 2$  dynes/cm and composed of brominated compounds, methylene chloride, and aromatic hydrocarbons, flowed from the fractures and wet the carbonate bedrock but formed beads on the water-wet stylolites, the interbedded silica deposits.

The wetting nature of the porous medium with respect to the NAPL depends on the electrostatic interactions between the NAPL-water interface and the water-mineral interface (Dubey and Doe 1993). When both the interfaces have like charges, the interfaces tend to repel each other and will produce water-wetness. However, in a situation where the interfaces have opposite charges, we will have an oil-wet regime. Alumino-silicate minerals have a tendency to show diverse behavior and exhibit different charges on different crystal faces. Due to this tendency, these minerals may exhibit weakly water wetting or oil-wetting characteristics under certain conditions. A change in the wettability may be achieved by changing the pH (Dubey and Doe 1993), by adsorption of a monolayer of polar molecules on the outer surface of the minerals (Morrow 1990), and contact of the mineral surfaces with acidic or basic organics (Powers et al. 1996). Hydrocarbons with higher molecular weights and higher boiling point fractions have a higher fraction of polar species and hence the ability to alter the wettability (Morrow 1990; Powers et al. 1996).

Chlorinated degreasing solvents will contain high molecular weight oils after they have been used for degreasing and possibly surface-active agents, such as alkaline detergents that may have been used to clean vapor degreasers. Any surface-active agents present have the ability to alter the electrostatic potential of the solvent-water interface and hence alter its wettability. The high molecular weight oils have the ability to coat mineral surfaces and achieve the same result, that is, a change from strongly water wet to mixed wet conditions.

Part of the problem in establishing the wettability of a geosystem is that the standard methods developed by petrophysicists have drawbacks. Lake (1989) points out

**Table 7**  
**Critical Trapping Numbers for Various Porous Media and Nonaqueous Phase Liquids**

Porous Medium	Nonaqueous Phase	Critical Trapping Number
Ottawa Sand <sup>1</sup>	PCE	$2 \times 10^{-5}$
Berea Sandstone <sup>2</sup>	Decne	$5 \times 10^{-6}$
Berea Sandstone <sup>3</sup>	Gas (c1/nC4)	$4 \times 10^{-6}$
Berea Sandstone <sup>4</sup>	Microemulsion	$3 \times 10^{-4}$
Hill Aquifer Material <sup>5</sup>	Hill DNAPL	$7 \times 10^{-3}$
<sup>1</sup> Pennell et al. 1996	<sup>2</sup> Delshad 1990	<sup>3</sup> Pope et. al. 1998
<sup>4</sup> Delshad 1990	<sup>5</sup> URS/DE&S 1998	

that although the Amott and the U.S. Bureau of Mines (USBM) methods provide a measure of the overall wettability of a core, these results are not correlated directly with any capillary pressure. The third method, the measurement of the contact angle of the wetting phase, requires measurement of a polished flat mineral surface in a vacuum. Such an environment bears little resemblance to the problem at hand.

Because of these drawbacks and because of the critical importance of wettability in the conduct of partitioning tracer tests, and water and surfactant floods, other means must be found to measure wettability. Capillary desaturation tests (Lake 1989) may provide an approach by which the issue of wettability can be examined from a purely practical standpoint of direct relevance to these injection-extraction operations. In fact, their first appearance in the literature of contaminant hydrogeology was in the context of the practicability of water-flooding NAPL zones (Wilson and Conrad 1984).

The main objective of conducting capillary desaturation experiments is to determine the critical trapping number, i.e., the total advective force (sum of both gravity and viscous forces) required to dislodge and mobilize trapped DNAPL. The advective and gravitational forces are described by the total trapping number developed by Pope of the University of Texas at Austin (Delshad et al. 1996; Pennell et al. 1996; see Appendix). The critical trapping number also provides insight into the wettability of the material being tested. A much larger trapping number is required to decrease the residual saturation of the wetting phase than the nonwetting phase (Pope et al. 1998; Delshad 1990). This is because the wetting phase preferentially occupies the smaller pores and has a tendency to coat the surfaces in the form of thin films (Powers et al. 1996). This means that a larger advective force is required to mobilize DNAPL if the mineral surfaces are oil-wet and translates into poorer DNAPL recoveries under oil-wet conditions.

Table 7 lists the critical trapping numbers for various porous media and different nonaqueous phases. The Berea sandstone cores in the presence of decane and gas and the Ottawa sand (Pennell et al. 1996) in the presence of technical-grade PCE were considered to be water wetting and have relatively low critical trapping numbers,

between  $10^{-5}$  and  $10^{-6}$ . The Hill aquifer material in the presence of Hill DNAPL (Table 4), however, and the Berea sandstone in the presence of surfactant-hydrocarbon microemulsion were observed to be rather weakly water wetting as evidenced by higher critical trapping numbers ( $3 \times 10^{-4}$  to  $7 \times 10^{-3}$ ). Because the Hill aquifer materials are >90% alumino-silicate minerals, such sediments would be expected to be strongly water wet with respect to chlorinated hydrocarbons as Pennell et al. (1996) showed. The fact that they appear at least partially DNAPL-wet and represent typical chlorinated degreasing solvents has important implications for DNAPL remediation.

## Conclusions

Because there are more than 20,000 vapor-degreasers in the United States, it appears likely that, due to the handling and disposal practices of the midcentury years, most if not all of these units will be identified in due course as sources of DNAPL contamination. Chlorinated degreasing solvents that are intentionally or accidentally released to the subsurface at these sites contain a number of toxic organic chemicals, not only the chlorinated hydrocarbons that make up the largest fraction of the solvent. Some of the additives included within chlorinated degreasing solvents are probably more toxic and certainly more mobile in ground water flow systems than are the chlorinated hydrocarbons themselves.

The process of vapor degreasing results in oil and grease accumulating in the solvent. Although this is self-evident, little thought has been given to the consequences of hydrophobic materials being present in chlorinated degreasing solvents. Most important of these is the issue of the state of wettability of the aquifer materials in contact with chlorinated degreasing solvents and the interfacial tension of the DNAPL with respect to the ground water. Both of these variables must be measured for the geosystem at each site prior to attempts at DNAPL removal. Assumptions regarding wettability and IFT must be recognized as such.

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## Biographical Sketches

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**Editor's Note** for "Chlorinated Degreasing Solvents: Physical-Chemical Properties Affecting Aquifer Contamination and Remediation" by R.E. Jackson, and V. Dwarakanath.

There had been a number of controversial issues and viewpoints expressed in this article and subsequent review comments. In the editor's opinion, the authors have done a good job of addressing reviewer concerns in the process of providing a critical examination of the practice of DNAPL detection and source remediation. *GWMR* appreciates the time and quality of the revised manuscript and the constructive comments of the reviewers.

—Michael J. Barcelona, Editor  
*Ground Water Monitoring and Remediation*

## Appendix: The Trapping Number

The trapping number was developed by Pope (Delshad et al. 1996; Pennell et al. 1996) for consideration of the total viscous, gravitational, and capillary forces acting on a trapped ganglia of NAPL held under capillary forces. The total trapping number is given by:

$$N_T = \sqrt{N_{Ca}^2 + 2N_{Ca}N_B \sin \alpha + N_B^2} \quad (1)$$

where  $N_T$  is the trapping number,  $N_{Ca}$  is the capillary number, and  $N_B$  is the bond number. For a porous medium in which  $k$  is the intrinsic permeability,  $k_{rw}$  is the relative permeability with respect to water, and  $\alpha$  is the angle the flow makes with the positive  $x$  axis (counterclockwise), we may define the capillary and bond numbers in terms of the magnitude of the Darcy velocity of the aqueous phase,  $q_w$ :

$$N_{Ca} = \frac{q_w \mu_w}{\sigma_{ow} \cos \theta} \quad N_B = \frac{\Delta \rho g k k_{rw}}{\sigma_{ow} \cos \theta} \quad (2)$$

$$|q_{w_i}| = \sqrt{q_w^2 + q_{w_z}^2} \quad (3)$$

where  $q_w$  is the dynamic viscosity of the aqueous phase,  $\Phi_{ow}$  is the interfacial tension (dynes/cm),  $\cos \theta$  is the contact angle formed by the grain surface and the wetting fluid,  $\Delta$  is the density difference between the DNAPL and ground water, and  $g$  is the gravitational constant.

Note that for the case of horizontal flow ( $\alpha = 0^\circ$ ), the expression for  $N_T$  reduces to:

$$N_T = \sqrt{N_{Ca}^2 + N_B^2} \quad (4)$$

and for vertical flow ( $\alpha = 90^\circ$ ), in the direction of the buoyancy force, the expression for  $N_T$  becomes:

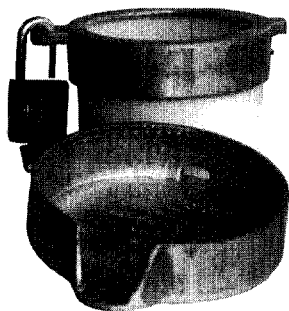
$$N_T = |N_{Ca} + N_B| \quad (5)$$



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